

# INVESTIGATION OF ELECTROCALORIC EFFECTS IN FERROELECTRIC SUBSTANCES

Status Report No. 7  
(Final Report)

March 1, 1967 to July 31, 1967

NASA Research Grant NsG-575

with

THE UNIVERSITY OF KANSAS  
Lawrence, Kansas

N67-39201

(ACCESSION NUMBER)

(THRU)

27  
(PAGES)

(CODE)

CP-89302  
(NASA CR OR TMX OR AD NUMBER)

06  
(CATEGORY)

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## GENERAL REMARKS ABOUT PYROELECTRIC CRYSTALS

The electrocaloric effect in crystalline tartaric acid was investigated because it is known to be pyroelectric. Pyroelectric substances presumably possess a spontaneous electrical polarization which, like the polarization in ferroelectric substances, is temperature dependent but unlike the polarization in ferroelectric substances is not reversible by the application of an electric field. The pyroelectric coefficient<sup>1</sup>  $p$  of tartaric acid is known to be large,<sup>2,3</sup>

$$p = (\partial P / \partial T)_E \approx (\partial D / \partial T)_{E=0} = 2.5 \times 10^{-5} \text{ coul/m}^2 \text{ deg},$$

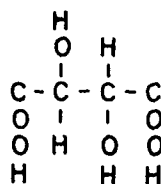
and this same coefficient appears in the  $dE$  form of the electrocaloric equation,

$$dT = - (T / \rho c_E) (\partial P / \partial T)_E dE. \quad (4)$$

We have already measured the electrical polarization of tartaric acid,<sup>3</sup> and found it to be much larger than other measurements would suggest.<sup>4</sup> Moreover, we expected that tartaric acid would have negligible dielectric hysteresis and that, with such a large spontaneous polarization, its electrocaloric behavior would be like that of a ferroelectric substance which had been electrically biased well into the strictly reversible region in the tail of its hysteresis cycle. This condition in which there is negligible motion of the domain walls (or perhaps no walls at all) is difficult to achieve in most ferroelectric substances even if high fields are applied.

The properties of tartaric acid are listed below. The dextro isomer was used.

Chemical formula:



Molecular weight = 150.1

Melting temperature = 170°C (443°K)

Specific Gravity = 1.759 ( $\rho$  = 1759 kg/m<sup>3</sup>)

Crystal class<sup>5</sup> = monoclinic sphenoidal; a:b:c = 1.275:1:1.027

Polar axis = along the y direction

Size of crystals = #53, 1.322 cm<sup>2</sup> x 2.29 mm; #51, 1.431 cm<sup>2</sup> x 2 mm

Electrodes = Air-drying silver paste, applied to entire area of the major faces

#### ELECTROCALORIC AND DIELECTRIC MEASUREMENTS OF TARTARIC ACID

Electrocaloric and static dielectric measurements were made on crystalline tartaric acid from 320.62°K to 91.10°K. The upper limit was imposed by our Woods-metal vacuum seals which melt at 69°C (342°K) and soften at a lower temperature. The lower limit was imposed by the diminution in both the electrocaloric effect and the sensitivity of the thermocouples that occurs as the temperature is lowered.

In the temperature range from 321°K down to 218°K, measurements of the changes in polarization and temperatures were observed for both stepwise and single-step changes in the applied field from zero to a maximum of 3,629 V/cm. The methods and apparatus used are described in earlier reports (Status Reports No. 1, 2, and 6).<sup>2,6,3</sup> Within this range the inner chamber which contains the crystal was filled with helium gas at atmospheric pressure in order to

prevent electrical arcing; the resulting conduction of heat violates the condition for an adiabatic process, but the "instantaneous" electrocaloric temperature changes could be read from the recorder trace without an appreciable correction. Typical results for the highest and lowest temperature within this upper range are shown in Figs. 1 and 2.

Below 218°K both the thermal noise due to the conductivity of the helium and the correction for non-adiabatic conditions become bothersome so the inner space was evacuated and the maximum field was reduced to half of its former value to avoid arcing. At these lower fields only one or two field steps were used in the interest of greater accuracy. Such measurements were made down to 91.10°K.

The linearity of both the changes in polarization and the electrocaloric effect with applied field is evident from Figs. 1 and 2. The linearity of the electrocaloric effect in tartaric acid is as expected, like the behavior of a ferroelectric substance biased to "saturation." However, the electrocaloric effect in a ferroelectric substance above its Curie temperature is a quadratic function of the applied field.

Figs. 1 and 2 show that the electrocaloric effect in tartaric acid reverses sign with the field as expected -- in contrast to the behavior of ferroelectric materials. Examination of the electrocaloric equation,

$$dT = - (T/\rho c_E) (\partial P/\partial T)_E dE, \quad (4)$$

reveals that unless  $(\partial P/\partial T)_E$  changes sign at  $E = 0$ , the result shown in Figs. 1 and 2 proves that the polarization of tartaric acid does not reverse under the influence of an applied field. An equivalent but simpler argument can be made on the basis of the conservation of entropy for an adiabatic process: when a positive field  $E$  is applied (in the direction of  $P$ ), it tends to decrease the entropy (increase the ordered polarization), so the temperature

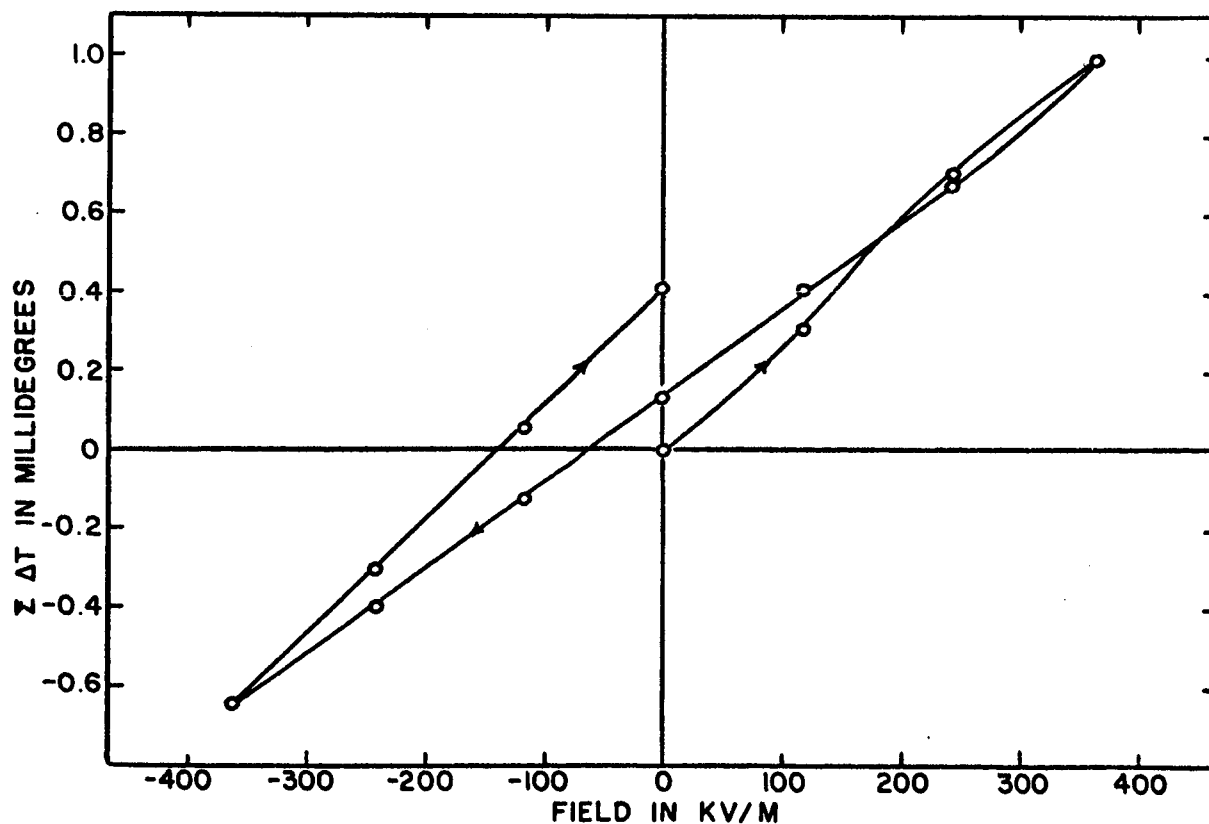
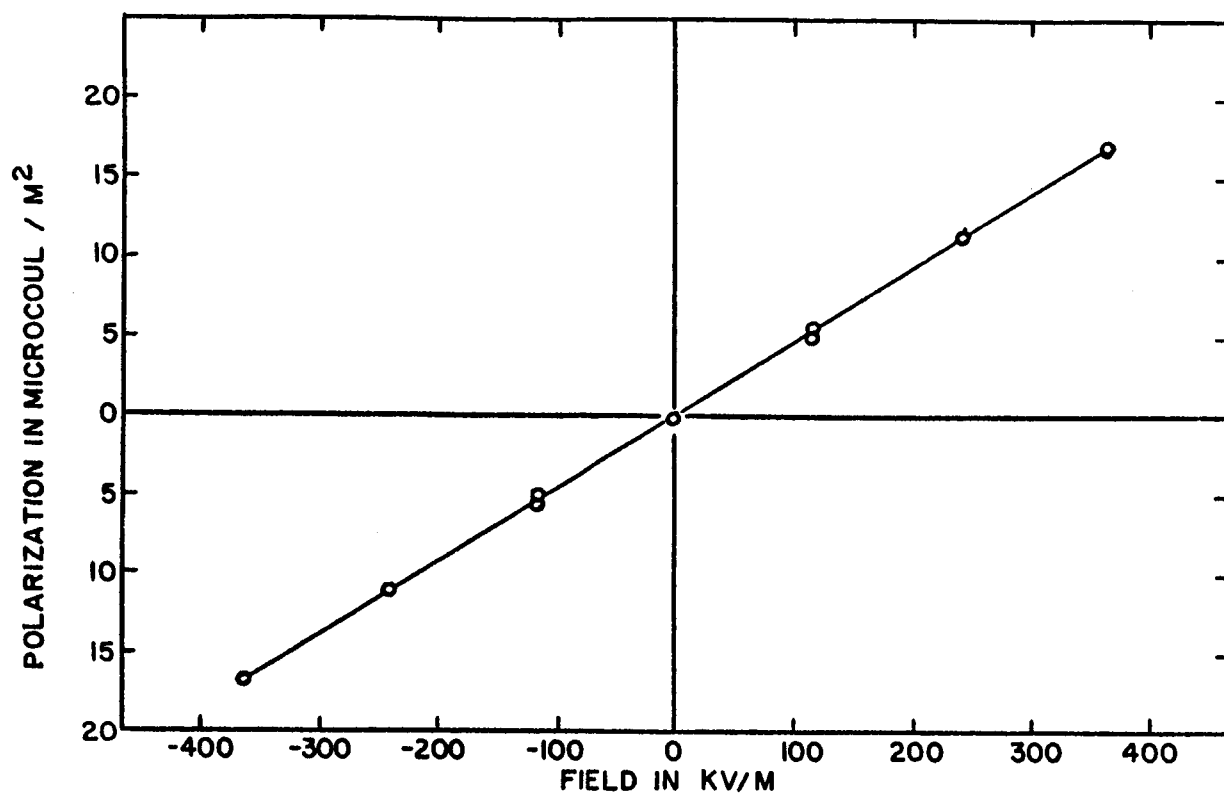


FIG.1 POLARIZATION AND ELECTROCALORIC EFFECTS IN TARTARIC ACID AT 218.85 °K

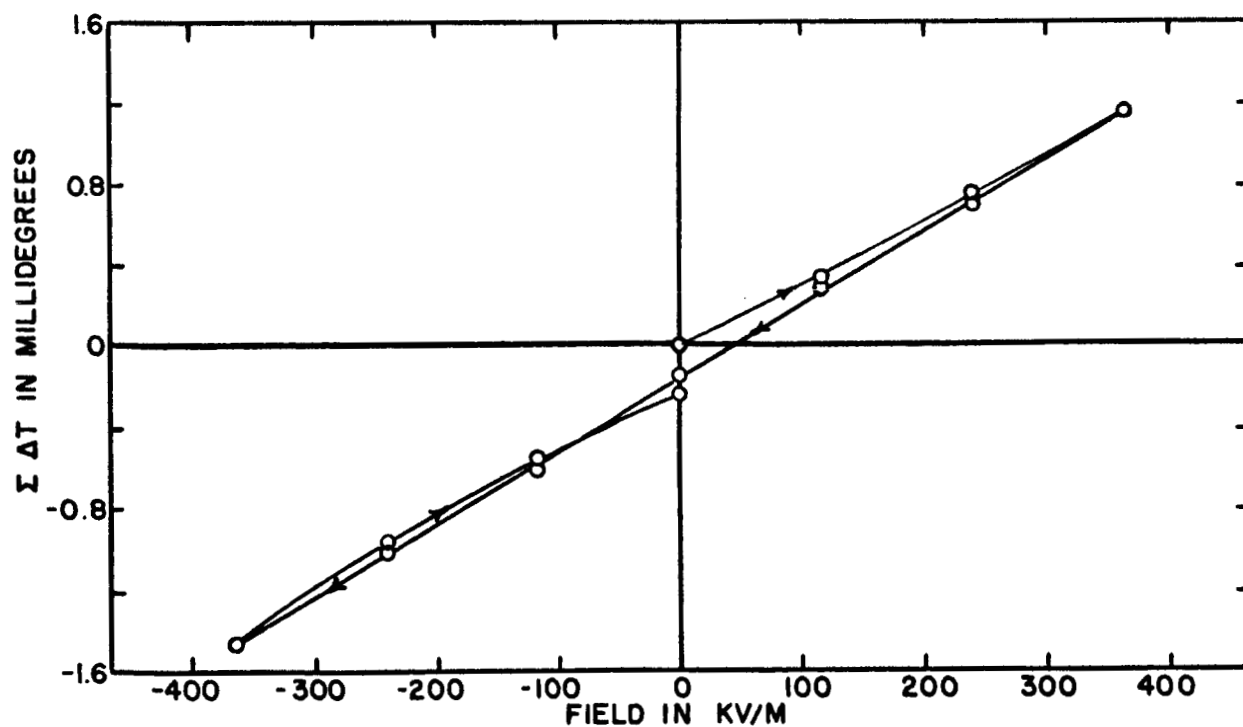
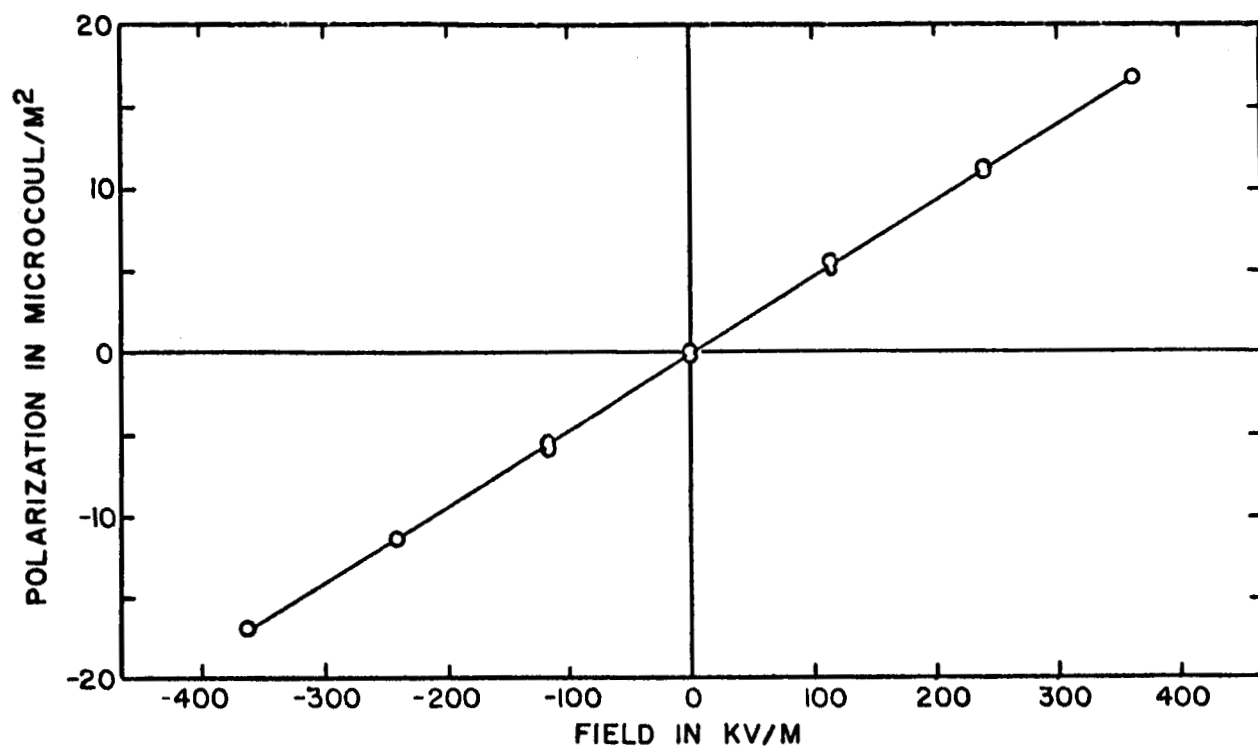


FIG. 2 POLARIZATION AND ELECTROCALORIC EFFECTS IN  
TARTARIC ACID AT 320.62°K

must rise in order to keep the total entropy of the crystal constant. Conversely, the temperature must fall to compensate for the disordering effect of a negative field. By contrast, a field of either direction tends to increase the order in a ferroelectric crystal which is compensated for by a rise in temperature.

A feeling for the relative magnitude of the field-induced polarization compared to the spontaneous polarization can be obtained from the following numbers:

<u>Temperature</u>	<u>Induced P</u>	
	<u>for E = 3 kV/cm</u>	<u>P<sub>s</sub></u>
90°K	13.5 $\mu\text{Coul}/\text{m}^2$	7,300 $\mu\text{Coul}/\text{m}^2$
300°K	13.5	3,670.

A surprising result was obtained for the static electric susceptibility of tartaric acid which was computed from the slopes of the plots of P vs E (e.g., Fig. 1 and 2);  $\Delta E/\Delta P$  turns out to be nearly constant over the entire range of temperature, a behavior which is distinctly different from that of a ferroelectric substance. Fig. 3 shows the values of  $\Delta P/\Delta E$  that were obtained at each temperature; the horizontal line represents the mean value of  $\Delta P/\Delta E$  and it corresponds to a differential dielectric constant of  $K = \Delta D/\epsilon_0 E = 5.22$  or a differential dielectric susceptibility  $\chi$  of 4.22. This value for K is somewhat larger than the value,  $K = 4.5$ , given by Mason,<sup>7</sup> but his value was evidently obtained at a frequency of 1000 cps so our "static" value should be higher than his. Mason's value for the temperature coefficient of K is  $1.9 \times 10^{-4}/^\circ\text{C}$  which is doubtfully perceptible in our measurements.



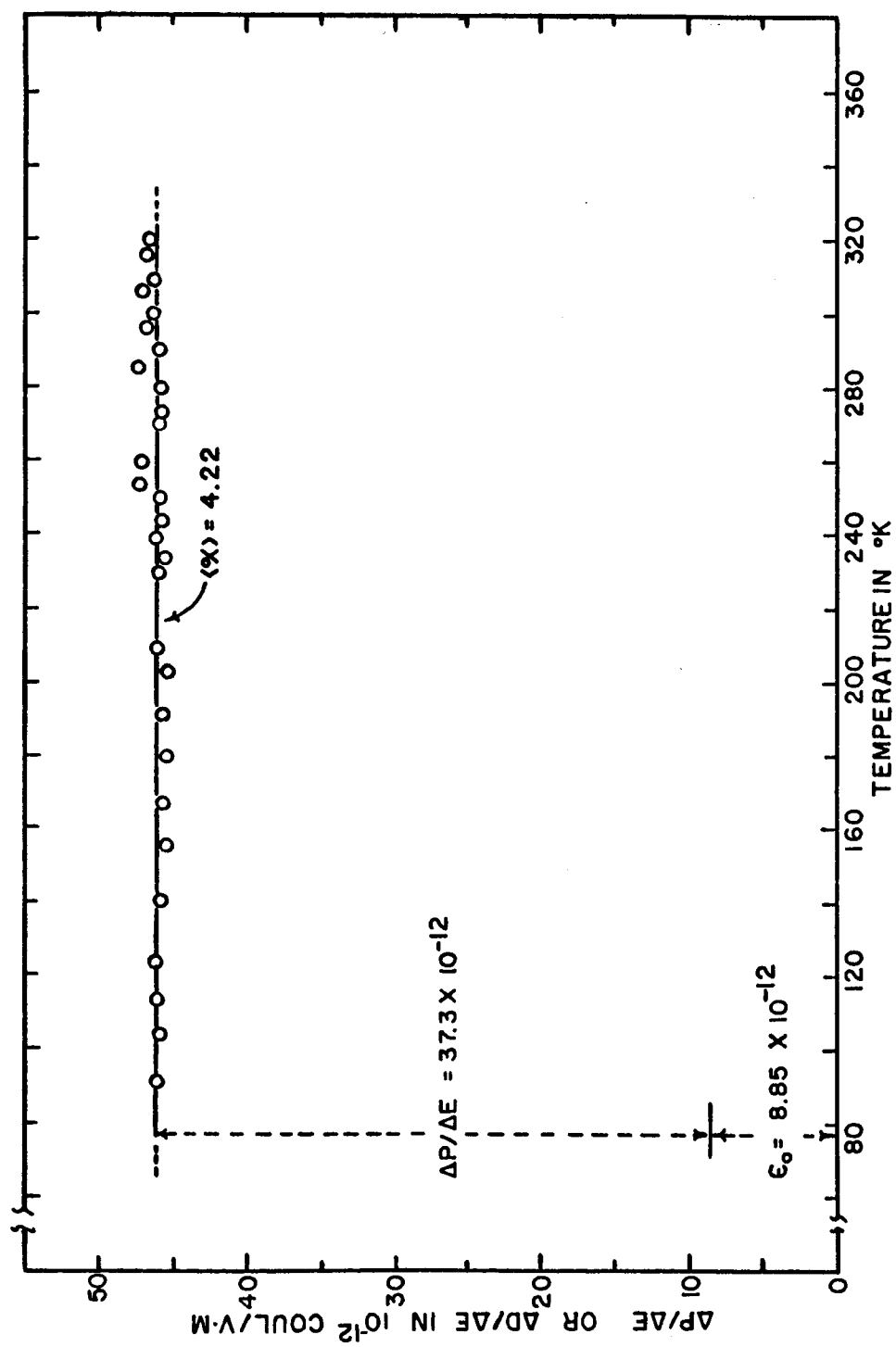


FIG. 3 POLARIZATION OF TARTARIC ACID INDUCED BY A STATIC FIELD

## AN EQUATION OF STATE FOR TARTARIC ACID

A quantitative comparison of the electrocaloric effect of a pyroelectric (or ferroelectric) crystal with other properties of the crystal requires some knowledge of the equation of state for that crystal, for example an equation giving the electrical polarization  $P$  as a function of temperature and applied electrical field. In the case of ferroelectric substance, the requisite relationships are difficult to measure, principally because the misalignment in the polarization of the various domains leads to spuriously small measured values and because not all combinations of state variables, such as  $P$  and  $T$ , are experimentally accessible.

On the other hand, since tartaric acid presumably does not break up into domains, there is a better chance to obtain valid measurements of  $P$  and then obtain an equation of state by fitting measured values to a physically reasonable analytic expression. In our case, a cue to obtaining such an analytical expression came from the well-known expression for the spontaneous polarization ferroelectric substance,

$$P_S^2 = -\omega/\xi, \quad (12)$$

where  $\omega$  is a Curie-Weiss term,  $(T-T_C)/\epsilon_0 C$ , and  $\xi$  is a constant for a substance which undergoes a second order transition. Accordingly, the measured values for  $P_S^2$  that we previously obtained for tartaric acid by the method of thermal depolarization<sup>3</sup> were plotted vs  $T$  with the result shown in Fig. 4. Besides exhibiting a linear relationship between  $P^2$  and  $T$ , a notable property of tartaric acid exhibited in Fig. 4 is the disappearance of the spontaneous polarization at a critical temperature  $T_C$ . We refrain from calling  $T_C$  a "Curie temperature" because we have no evidence that the crystal obeys a Curie-Weiss law above  $T_C$ ; in fact, the crystal rapidly becomes electrically conductive as it approaches  $T_C$ . Except in the region close to the critical temperature  $T_C$ ,

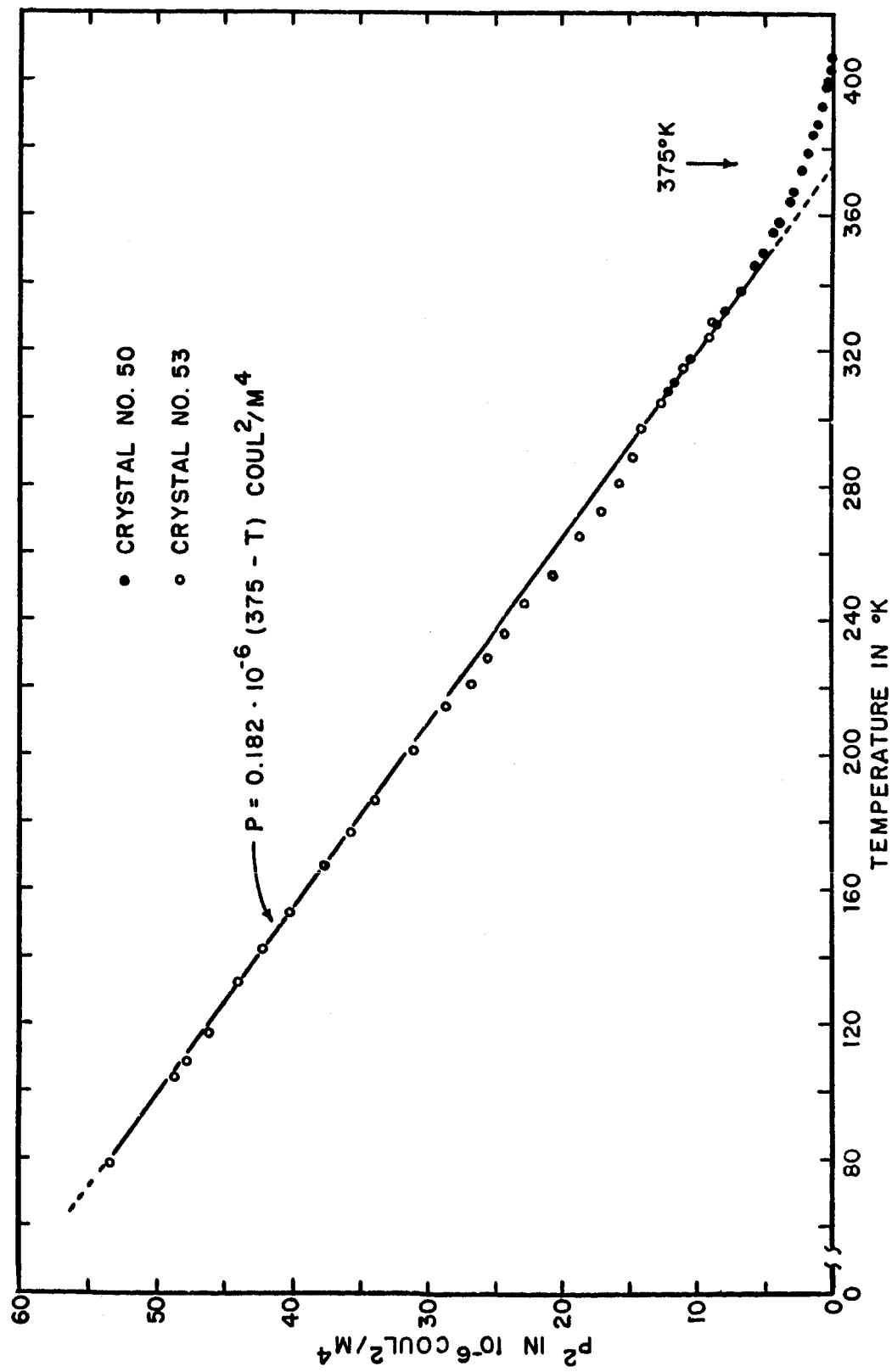


FIG. 4 SPONTANEOUS POLARIZATION OF TARTARIC ACID DETERMINED  
 BY THERMAL DEPOLARIZATION

the spontaneous polarization of tartaric acid as a function of temperature is well represented by a linear expression in the temperature,

$$P_s^2 = 0.182 \times 10^{-6} (375 - T) \text{ Coul}^2/\text{m}^4.$$

An expression for the field-induced polarization of tartaric acid can be obtained directly from the experimental values presented in Fig. 3; it is

$$\Delta P = 37.3 \times 10^{-12} \Delta E.$$

At this point we assume that the values of  $(\partial E/\partial P)$  at constant entropy and at constant temperature are practically the same, a result that can be verified later from the observation that the electrocaloric temperature changes are only about one millidegree; i.e., we presume that  $(\partial P/\partial E)_T = 37.3 \times 10^{-12}$ .

Integration of the above expression gives an equation of the form

$$P = BE + \phi(T)$$

where  $B$  is the constant  $37.3 \times 10^{-12}$ , and  $\phi(T)$  is an arbitrary function of temperature. Knowing that  $P$  approaches  $P_s(T)$  as  $E$  approaches zero, and employing the experimental values for  $P_s(T)$  shown in Fig. 4, we have

$$P = BE + A(T_c - T)^{1/2} \quad (40)$$

where  $A = (0.182 \times 10^{-6})^{1/2} = 0.426 \times 10^{-3} \text{ Coul/m}^2 \cdot \text{deg}^{1/2}$ ,

and  $B = 37.3 \times 10^{-12} \text{ Coul}^2/\text{N} \cdot \text{m}^2$ .

This is the equation of state for tartaric acid in the region of interest except for the region close to the critical temperature.

# THE GIBBS FREE ENERGY OF TARTARIC ACID

It is instructive to see whether Eq. (4) leads to a physically reasonable expression for the Gibbs free energy.

Combining Eq. (7) and (40), we have

$$(\partial G / \partial P)_T = (P/B) - (A/B) (T_c - T)^{1/2}.$$

Integration of this expression gives

$$G_1 = G_{10} - (A/B)(T_c - T)^{1/2} P + P^2/2B \quad (41)$$

where  $G_{10}$  is the free energy of an unpolarized crystal at the temperature  $T$ .

The salient feature of the above expression is that it is an odd function of the polarization in contrast to the analagous expression for the Gibbs free energy of a ferroelectric crystal.<sup>2</sup> The free energy of a well-behaved ferroelectric substance such as triglycine sulfate which undergoes a second-order transition is<sup>8</sup>

$$G_1 = G_{10} + [(T - T_c)/\epsilon_0 e] P^2/2 + \xi P^4/4. \quad (8a)$$

This odd function for  $P$  might have been expected because the even function that is written for a ferroelectric crystal describes the symmetrical reversibility of the direction of its polarization whereas the polarization of a pyroelectric crystal does not reverse. The qualitative behaviors of the even and odd functions of polarization at temperatures below the critical temperature are shown below. (Compare these to the diagrams on page 8 of Report No. 1.) In both the ferroelectric and pyroelectric crystals the magnitude of the lower-order (negative) term diminishes with increasing temperature until at some critical temperature the spontaneous polarization in the stable state (the state of minimum free energy) diminishes to zero. An

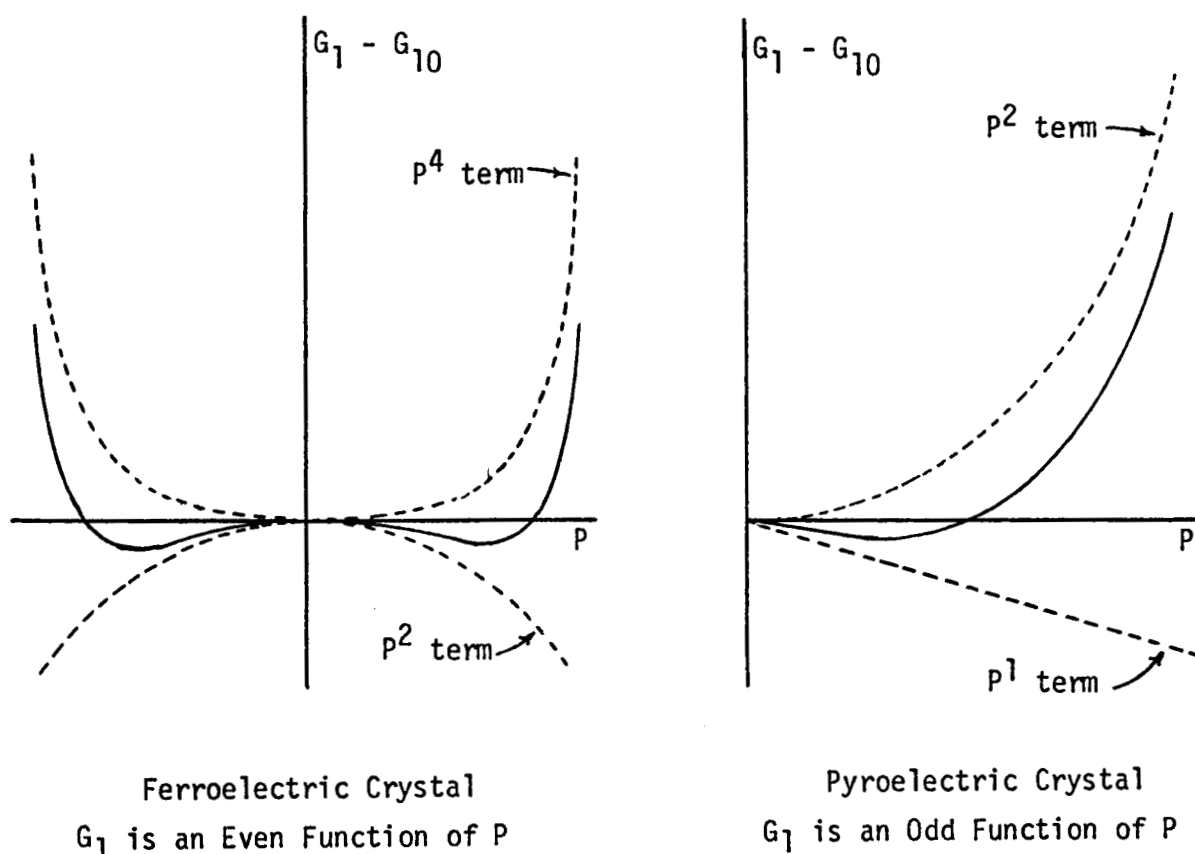


Fig. 5. A qualitative Comparison of the Even and Odd Functions of Polarization that Describe the Free Energy of Ferroelectric Pyroelectric Crystals.

important difference between these free energy functions is that Eq. (8a) for a ferroelectric crystal predicts correctly that the reciprocal isothermal susceptibility,  $1/\chi^T = \epsilon_0(\partial^2 G_1 / \partial P^2)_T$  approaches zero at the critical temperature whereas Eq. (41) for a pyroelectric crystal predicts that the isothermal susceptibility will be constant right up to the critical temperature. We did not verify this prediction by extending our susceptibility measurements (Figs. 1 and 2) to the critical temperature (375°K) because of the low melting point of our Woods metal seals and because other measurements showed that the conductivity

increases rapidly in this region.

### THE ELECTROCALORIC EFFECT IN TARTARIC ACID

The electrocaloric effect in crystalline tartaric acid was measured at fields up to 3,629 V/cm from 320.62°K down to 218.85°K and at fields up to 1,790 V/cm at temperatures down to 91.10°K. The typical results of these measurements, displayed in Figs. 1 and 2, show that the processes are practically reversible in the thermodynamic sense and that the temperature changes were significantly smaller than those ordinarily obtained with ferroelectric substances.

If the general considerations already outlined are correct, in particular if Eq. (41) for the Gibbs free energy is correct, then measured values of the electrocaloric effect should agree with the values that can be predicted from the general thermodynamic equation,

$$dT = - (T/\rho c_E) (\partial P/\partial T)_E dE. \quad (4)$$

But from Eq. (41) or from the equation of state we have

$$(\partial P/\partial T)_E = -(A/2)(T_C - T)^{-1/2}.$$

If this expression is substituted into Eq. (41) and if Eq. (4) is integrated while assuming that the electrocaloric temperature change is much smaller than  $T$  the result is

$$\Delta T = (AT/\rho c_E)(T_C - T)^{-1/2} \Delta E. \quad (42)$$

Unfortunately, the published values for  $c_E$ , the heat capacity of tartaric acid, do not cover the full range of temperatures needed here and they are not in good agreement with each other. Our efforts to construct an adiabatic

calorimeter to make these measurements are not complete, therefore we must rely on the published values.<sup>9,10,11</sup> These values are shown in Fig. 6, the horizontal lines in the figure representing the temperature ranges over which the various authors made their measurements. A straight line was drawn to represent the values used for our calculations, extra weight being given to the values at 309.2°K and 323°K because of their consistency. The value at 301.5° was ignored because it is anomalously high. The resulting linear relationship that was used is

$$c_E = 120 + 3.50T \text{ Joules/kg} \cdot \text{deg.}$$

Fig. 7 was drawn to compare the the measured values of the electrocaloric effect and the values calculated from Eq. (42). The agreement is better than we have a right to expect, especially near 300°K where the two published values of the heat capacity are in agreement, but the curvature of the patterns of the experimental and calculated values appear to be opposite to each other. Electrocaloric measurements at higher temperature (if they are possible) and better values for the specific heat are required to verify this trend. Values at much lower temperatures would be difficult to measure because the measured thermal emf becomes smaller. Thermal emf's for  $10^{-4}$ °K are shown for several temperatures in Fig. 7.

Our conclusion is that Eq. (41) is a reasonable quantitative representation of the Gibbs free energy of tartaric acid from 90°K to 320°K.

We have not made electrocaloric measurements between 320°K and 375°K and are not able to explain the significance of the deviation of  $P_S^2$  from linearity in T that is evident in Fig. 4. Part of the deviation could be due to a small error in determining  $P_S$ ; only changes in  $P_S$  can be measured by the method of thermal depolarization, and it is difficult to tell when the thermal depolarization currents actually become zero.<sup>3</sup>



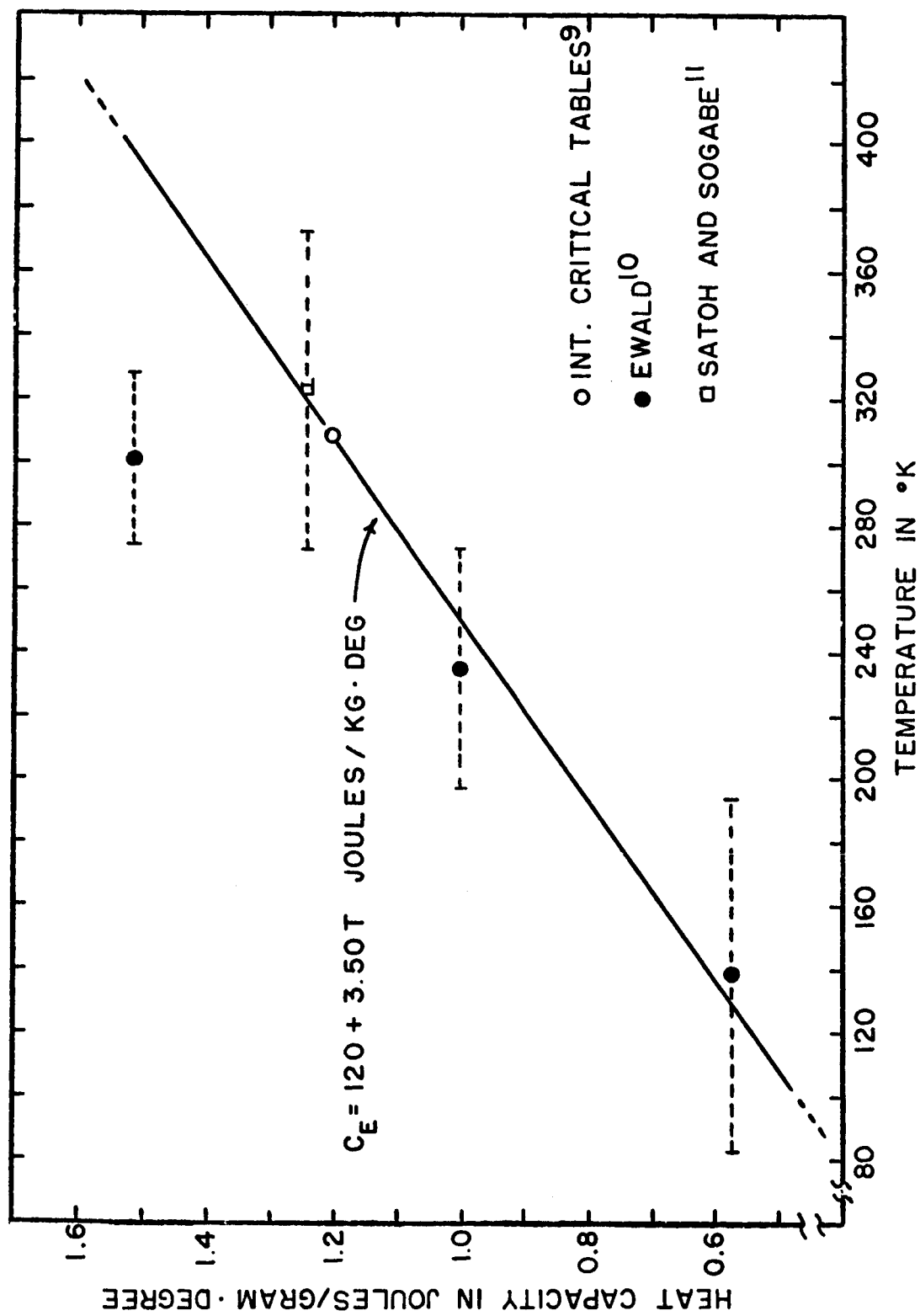


FIG. 6 PUBLISHED VALUES FOR THE HEAT CAPACITY OF TARTARIC ACID

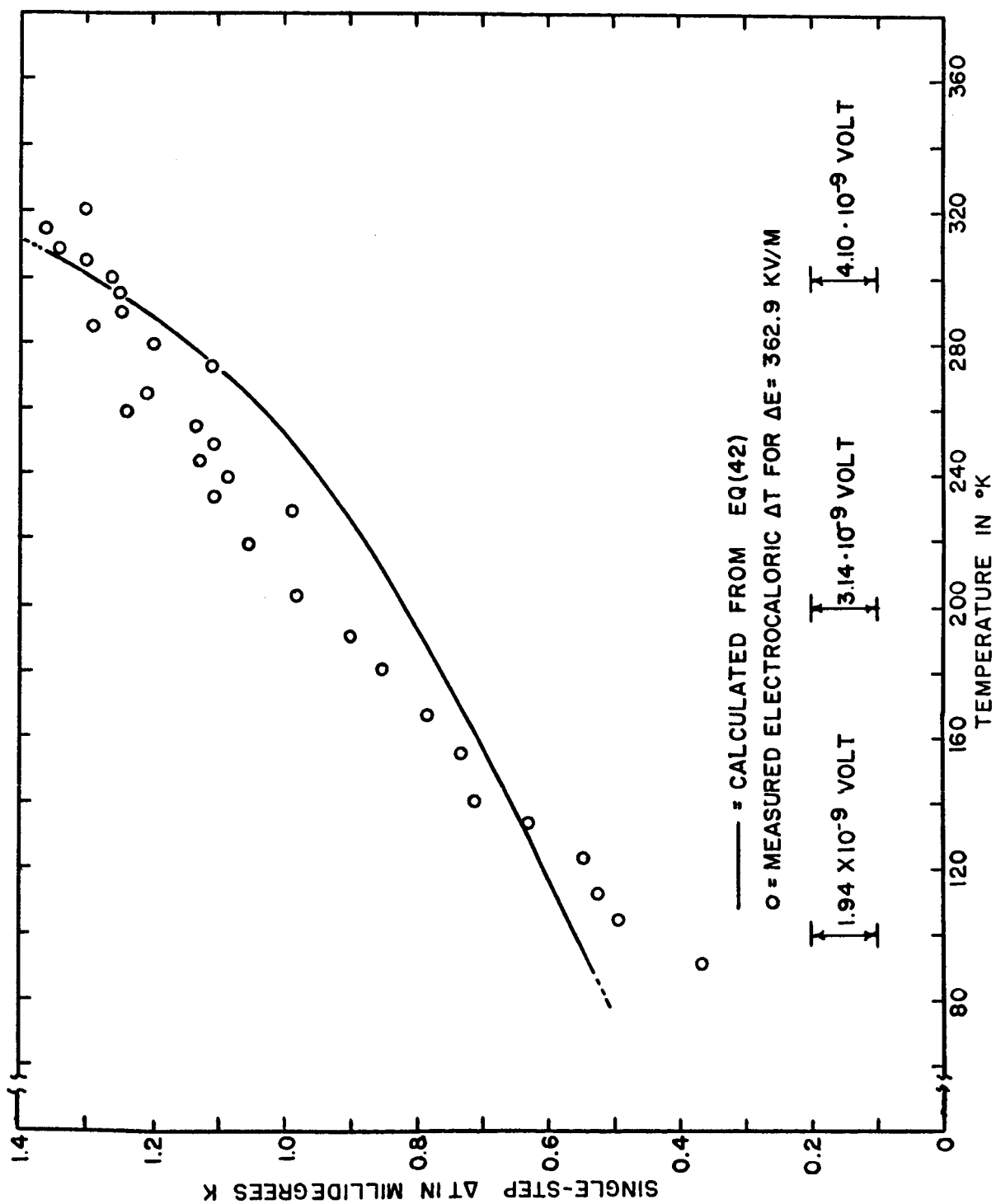


FIG. 7 MEASURED VS. THEORETICAL ELECTROCALORIC EFFECTS  
 IN TARTARIC ACID

## ATTEMPTS TO GROW OTHER CRYSTALS

Crystal growing has been a bottleneck. Attempts to grow better crystals of ammonium hydrogen sulfate<sup>3</sup>  $(\text{NH}_4)\text{HSO}_4$  were continued, and although improved crystals were obtained and installed in our measuring equipment, they proved to be too conductive for valid measurements of the electrocaloric effect. Both we and the Harshaw Chemical Company were unable to grow satisfactory crystals of diglycine nitrate  $(\text{NH}_2\text{CH}_2\text{COOH})_2 \cdot \text{HNO}_3$ . We also made a supply of methylammonium aluminum sulfate dodecahydrate from which some seed crystals have been obtained, but we have not produced any large specimens. Likewise, good seeds of lithium sulfate monohydrate were obtained, but large crystals have not yet been grown.

## SUMMARY OF RESULTS FOR THIS PERIOD

Measurements of the electrocaloric effect and the static dielectric properties of crystalline tartaric acid were found to be quantitatively consistent with the generally-held idea that the pyroelectric effect is due to a large temperature-dependent spontaneous polarization that is masked by conduction charges until it is changed by a change in temperature and that the spontaneous polarization of a pyroelectric substance is somewhat like that of a ferroelectric substance but is not reversible by an electric field.

An equation of state and an expression for the Gibbs free energy for unstressed tartaric acid were deduced from the experiments. They are

$$P = +A(T_0 - T)^{1/2} + BE, \quad (40)$$

and 
$$G = G_{10} - (A/B)(T_0 - T)^{1/2}P + P^2/2B. \quad (41)$$

The numerical values of the coefficients were found to be

$$A = 0.426 \times 10^{-3} \text{ Coul/m}^2 \cdot \text{deg}^{1/2},$$

and 
$$B = 37.3 \times 10^{-12} \text{ Coul}^2/\text{n} \cdot \text{m}^2.$$

### SUMMARY OF PREVIOUS STATUS REPORTS

Status Report No. 1 contains a thermodynamic description of the electrocaloric effect, the pyroelectric effect, and the relationship between them.<sup>2</sup> Such a description includes the proposition that both effects arise from the same crystalline properties and that the relevant thermodynamic coefficients can be determined from measurements of the electrocaloric effect. So-called "tertiary effects," which arise from temperature gradients or fields and can be so large that they mask the real effects, are more easily eliminated from the electrocaloric measurements than from the pyroelectric measurements.

The apparatus and techniques that were devised for regulating accurately the temperature of the experimental chamber and for making simultaneous measurements of the changes in electric polarization and temperature that occur with changes in applied field were described.

Status Report No. 2 included an account of the measurements of the electrocaloric effect in  $\text{KH}_2\text{PO}_4$  over the temperature range from 78°K to 136°K.<sup>6</sup> Numerical values for the pyroelectric coefficient and its variation with temperature were determined from the measured electrocaloric effect. Reliable values for the Devonshire coefficients could not be determined from the electrocaloric effect because their determination depends upon measured values of changes in polarization, and the polarization of  $\text{KH}_2\text{PO}_4$  is nearly saturated in the nearly-reversible tail of the hysteresis loops where the electrocaloric measurements. (E.g., see Fig. 4 of Status Report No. 2.)

Report No. 3 describes the changes in the apparatus and techniques that were made to permit measurements of changes of polarization in the nearly-

reversible tails of the hysteresis loops (i.e., in the "saturation" region).<sup>12</sup> These changes included the use of (1) a well-regulated, high-voltage d-c power supply, (2) a much more sensitive d-c amplifier with a much higher input resistance for measurements of polarization, and (3) a charge-biasing procedure to suppress the zero of the charge-measuring equipment. Measurements of both  $\Delta T/\Delta P$  and  $\Delta T/\Delta E$  were made for potassium dihydrogen phosphate over the entire temperature range for which the electrocaloric effect is appreciable, 77°K to 136°K. These measurements show that maximum sensitivity for low-impedance pyroelectric detectors used in the ferroelectric state is not obtained until the applied biasing field is sufficiently large to bring the specimen into the nearly-reversible tail of the hysteresis loop. The sensitivity of a pyroelectric detector operated in the paraelectric state, can be controlled over a wide range by a suitable biasing field, the sensitivity increasing with the field.

A relatively simple expression was found which gave a good fit to measured values of  $(\Delta T/\Delta P)_S$  for  $\text{KH}_2\text{PO}_4$  over the entire temperature range, right through the Curie temperature. It is

$$(\partial E/\partial P)_T = (\rho C_P/T)(\Delta T/\Delta P)_S = 3.63 \times 10^7 P = 4.80 \times 10^{12} P^5.$$

On the other hand, a Gibbs function  $G_1$  that accurately describes both the ferroelectric behavior and the pyroelectric coefficient over the entire range of temperatures could not be found.

The variation with temperature and field of an inner field coefficient  $\gamma$  that can be used to describe the spontaneous polarization and the electrocaloric effect in  $\text{KH}_2\text{PO}_4$  was determined.

A computer program using Fortran IV was written for an IBM 7040 computer; its use vastly increased the speed and accuracy of some of the tedious computations and curve-plotting.

Status Report No. 4 is an account of the electrocaloric effect in triglycine sulfate,  $(\text{NH}_2\text{CH}_2\text{COOH})_3 \cdot \text{H}_2\text{SO}_4$  throughout the temperature range over which an appreciable effect exists, 273°K to 334°K, and at electric fields up to 306 kv/m. This material has a large pyroelectric coefficient especially near the Curie temperature (322.6°K or 49.45°C) as expected. The first Devonshire coefficient  $\omega$  was found to be a continuous function of temperature with no change in slope right through the Curie temperature, a behavior to be expected of a second-order ferroelectric transition. Because of the relatively high temperature at which the electrocaloric effect occurs in this substance, relaxation polarization and/or ohmic conductivity effects are so large that they prevent an accurate determination of the second Devonshire coefficient.

The pyroelectric coefficient of triglycine sulfate was determined from the electrocaloric measurements. It is a strong function of temperature. It is nearly independent of field below the Curie temperature, but it can be controlled by adjusting the field above the Curie temperature.

Status Report No. 5 includes an account of the electrocaloric effect in crystalline potassium dihydrogen arsenate  $\text{KH}_2\text{AsO}_4$  throughout the range over which the effect is appreciable, from 80.45°K to 100.57°K which includes the transition temperature.<sup>13</sup> This material is similar to potassium dihydrogen phosphate in both its electrocaloric and dielectric properties. The first Devonshire coefficient  $\omega$  is not a smooth function of temperature throughout the transition region, and no analytical expression for the elastic Gibbs function  $G_1$  was found that would describe the crystal both above and below the Curie temperature. Both the static dielectric measurements and the electrocaloric measurements taken in the nearly-reversible tails of the hysteresis loops gave evidence for believing that the ferroelectric transition in  $\text{KH}_2\text{AsO}_4$  is of first-order rather than second-order. Qualitative cooling curves

taken of a short-circuited single crystal also supported this belief and were at variance with specific heat measurements reported for open-circuited polycrystalline specimens.

Report No. 6 describes the method of "thermal depolarization" that can be used to measure spontaneous polarization.<sup>3</sup> The method was tested on ferroelectric triglycine nitrate for which the spontaneous polarization is known from dielectric hysteresis measurements and found to be valid. The method was then used to measure the spontaneous polarization of tartaric acid, and it produced values for  $P_s$  much larger than the published values for other pyroelectric substances. (Published values of  $P_s$  for tartaric acid were not found.)

This report also contains an account of experiments which showed that crystals with vacuum-plated metal electrodes exhibit higher (and presumably better) values of polarization than do crystals with metal foil or silver paste electrodes, 3% to 10% higher for crystals of triglycine sulfate at 60 cps.

## APPENDIX A: DEFINITIONS OF TERMS AND SYMBOLS

Rationalized MKS units are used throughout. Thermodynamic formulas such as  $dU = TdS + Xdx + EdP$  are written for a unit volume of material. This procedure is not exactly proper because the thermodynamic system (the experimental crystal) changes its volume slightly, but only inappreciable errors result.

$C$  = Curie constant. Curie-Weiss Law is  $\chi = C/(T - T_p)$ .

$c_E$  = Specific heat at constant field (and zero stress).

$c_p$  = Specific heat at constant polarization (and zero stress).

$D$  = Electric displacement.  $D = \epsilon_0 E + P$ .

$E$  = Applied electric field.

$G_1$  = Elastic Gibbs function.  $G_1 = U - TS - xX$ .

$G_{10} = G_1$  at some (arbitrary) reference temperature.

$p$  = Electric dipole moment.

$P$  = Electric polarization per volume.  $P_s$  is the spontaneous electric polarization per volume.

$p^E$  = Pyroelectric coefficient at constant field (and stress).

$S$  = Entropy per volume.

$T$  = Temperature in degrees Kelvin.

$T_c$  = Critical temperature. Loosely speaking, either  $T_f$  or  $T_p$  for a ferroelectric substance. The temperature at which  $P_s$  approaches zero in a pyroelectric substance.

$T_f$  = Ferroelectric Curie temperature = the temperature at which  $P_s$  disappears when the substance is heated.

$T_p$  = Paraelectric Curie temperature as defined by the Curie-Weiss Law,

$$\chi = C/(T - T_p).$$



$U$  = Internal energy per volume.

$X$  = Applied stress. (Tensile stress has a positive sign.)

$x$  = Strain. (Elongation has a positive sign.)

$\epsilon_0$  = Electric permittivity of vacuum =  $8.85 \times 10^{-12}$  coul<sup>2</sup>/n.m<sup>2</sup>.

$\zeta$  = Devonshire's sixth-order coefficient (of  $P^6$ ) in G-expansion.

$\xi$  = Devonshire's fourth-order coefficient (of  $P^4$ ) in G-expansion.

( $\psi$  appears as a misprint in place of  $\xi$  in Eq. 7 and 9 of Status Report No. 1.)

$\rho$  = Mass density.

$\chi$  = Electric susceptibility.  $dP = \epsilon_0 \chi dE$ . The symbol  $\chi$  may carry subscripts as  $p$  (paraelectric), or superscripts such as  $T$  (constant temperature),  $X$  (constant stress), etc.

$\psi$  = The non-linear polarization function in the Devonshire expansion.

Usually written  $\psi(P)$ .

$\psi'$  = The derivative of  $\psi(P)$  with respect to  $P$ . Usually written  $\psi'(P)$ .

$\omega$  = Devonshire's second-order coefficient (of  $P^2$ ) in G-expansion.

## APPENDIX B: LIST OF EQUATIONS

A list of the most important equations from previous reports is given below. All equations are numbered consecutively, as they first appeared in these reports.

$$dU = TdS + Xdx + EdP \quad (1)$$

$$dT = (T/\rho c_p)(\partial E/\partial T)_p dP \quad (2)$$

$$dT = -(T/\rho c_E)(\partial P/\partial T)_E dE \quad (4)$$

$$P = f(a) = f[p(E + \gamma P)/kT] \quad (5)$$

$$dT = (\gamma/\rho c_p)PdP \quad (6)$$

$$dG_1 = -SdT = x dX + EdP \quad (7)$$

$$G_1 = G_{10} + \omega P^2/2 + \xi P^4/4 + \zeta P^6/6 \quad (8)$$

$$(\partial G_1 / \partial P)_T = E = \omega(T)P + \xi P^3 + \zeta P^5 \quad (9)$$

$$dP = p^{X,E} dT \quad \text{where } p^{X,E} = (\partial P / \partial T)_{X,E}. \quad (20)$$

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